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ABSTRACT

The authors discuss phase diagrams of the hafnium-tantalum system in the solid state. They present X-ray diffraction patterns of the various alloys with α, β, ω single- and two-phase regions.

The literature contains no available data on phase diagrams of /206* the hafnium-tantalum system. Only reference 1 mentions the X-ray diffraction investigation of one of the $HfTa_2$ composition alloys after 10-minute annealing at 800°C. This alloy had a two-phase structure. One phase had a body-centered cubic lattice and the other had a hexagonal lattice structure.

According to well-agreeing data of different investigators, the melting point of tantalum is 2996-3000°C. Various data on the determination of the melting point of hafnium are in much less agreement. The following values of the melting point of hafnium were published (in °C): 2230 ± 50 (ref. 2), 2130 ± 15 (ref. 3), 1975 ± 30 (ref. 4), 2235 ± 5 (ref. 5), 2222 ± 30 (ref. 6), 2150 (ref. 7) and 2190 ± 20 (ref. 8). These great discrepancies can be explained by the difficulties of obtaining hafnium sufficiently free from admixtures, particularly zirconium. This metal has a concentration varying

*Numbers given in margin indicate pagination in original foreign text.

in different grades of hafnium from 0.7 to 4 percent. The discrepancies between the values established by different authors for the temperature of polymorphic transformation in hafnium are just as large as for the melting point. The following values were published for this temperature (in °C): 1327-1527 (ref. 9), 1310 ± 10 (ref. 10), 1950 ± 100 (ref. 11), 1760 ± 35 (ref. 12), 1750 ± 20 (ref. 13), 1660 (ref. 14), 1730 (ref. 15) and 1735 (ref. 16). Apparently the most reliable are the values 2222 ± 30°C for the melting point and 1760 ± 35°C for the temperature of polymorphic transformation, since these values were obtained with the purest hafnium.

Production, Heat Treatment and Method of Investigation of Alloys

Alloys were prepared from sintered tantalum and hafnium iodide remelted in an electron beam furnace. The alloys were prepared in an arc furnace with a permanent tungsten electrode on a water-cooled copper base in an argon atmosphere. Argon was purified by melting a titanium-zirconium alloy /207 getter (50 percent Ti and 50 percent Zr). Uniformity in the composition of ingots was insured by 4-5-fold remelting, during which the ingots were turned after each melting. Verification of the alloy composition was conducted by comparing the weight of the batch and the final weight of the melt. An insignificant difference in these weights indicated that the composition of the produced alloys differed from the compounded batch by not more than 1 percent.

All alloys were subjected to annealing according to the following schedule: 1500°C--50 hr, 1300°C--63 hr, 1100°C--100 hr and 900°C--150 hr. Thermal and dilatometric analysis of the alloys were conducted on the instrument described in reference 17. Tempering of the alloys from high temperatures was conducted on a special apparatus. A batch of up to 30 specimens, 7 mm in diameter and 8 mm in height, was heated in the purified argon

atmosphere. The temperature of the specimens during heating and prior to tempering was controlled with a VR-5/20 thermocouple. The specimens were quenched in oil. The maximum temperature to which the specimens were heated prior to tempering was 1900°C. Tempering of shavings of specimens was conducted in the same apparatus. Shavings were placed into molybdenum crucibles and closed with covers.

X-ray powder diffraction patterns of alloys were obtained by the use of a URS-70 instrument in an RKD camera using chromium K_α radiation.

Experimental Results

Sixteen binary alloys were prepared. Their starting batch composition is given in the table. All alloys were relatively hard and viscous and were very difficult to file or to machine with a cutting tool.

The microstructures of cast alloys indicate a decomposition of the solid solution (fig. 1).

Alloys Nos. 4, 7, 9, 10 and 11 were subjected to thermal analysis by heating to 1600-1800°C. These operations gave no signs of melting, although at 1000-1050°C solid-state endothermic transformation was detected. A more accurate value of the temperature of this transformation was determined by dilatometric analysis. For alloys Nos. 3, 5 and 8 the following values of /208 transformation temperature were obtained: 1040, 1022 and 1020°C. Figure 2 shows a dilatogram for heating alloy No. 8. Transformation begins at 1020°C and is accompanied by contraction of the specimen.

Alloys annealed at different temperatures were subjected to X-ray phase analysis. Here it was discovered that in alloys, annealed at 1300 and 1500°C, there was decomposition of the solid solution during cooling, since the cooling

No. of alloy	Concentration of Ta, wt %	No. of alloy	Concentration of Ta, wt %	No. of alloy	Concentration of Ta, wt %
1	2.5	6	20	11	70
2	5.0	7	30	12	75
3	7.5	8	40	13	80
4	10	9	50	14	85
5	15	10	60	15	90
				16	95

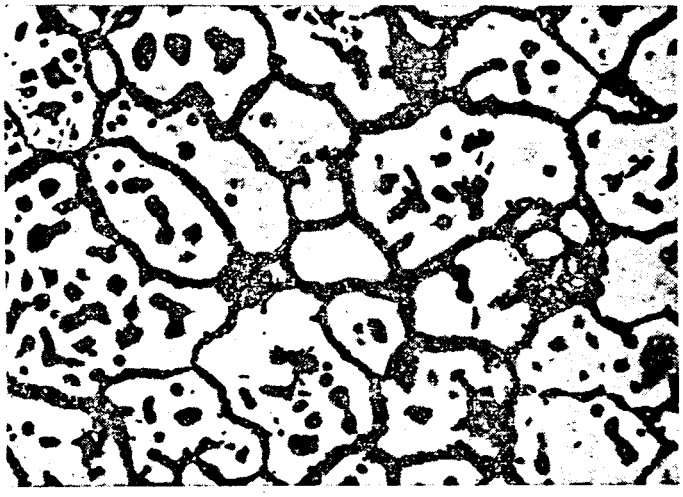

Figure 1. Microstructure of cast alloy No. 10 (thermal etching, × 350.

rate of alloys in the TVV-2M furnace is insufficient to suppress these processes. In order to establish structures which correspond to the equilibrium at 1300 and 1500°C alloy powders were tempered from these temperatures. As a

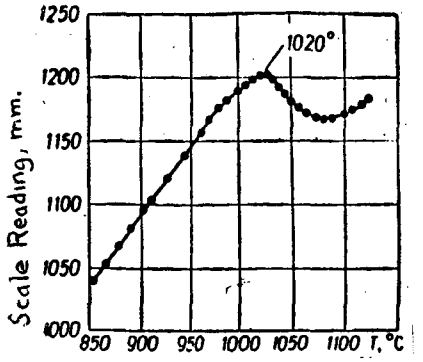

Figure 2. Dilatogram for heating alloy No. 8.

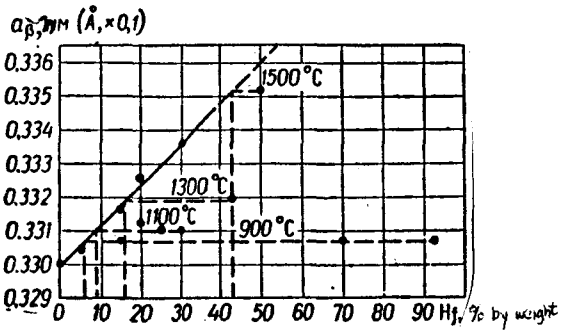

Figure 3. Lattice parameter of β_2 phase as function of temperature of annealing and concentration of hafnium.

result it was possible to obtain a stable, supersaturated β_2-phase at room temperature (solid solution of hafnium in tantalum) and, having determined its crystal lattice parameter, to construct a calibration graph for determination of limiting solubility of hafnium in tantalum at the selected temperatures. Figure 3 shows a calibration graph and values of lattice parameters of the β_2-phase for alloys annealed in the two-phase (β_1 + β_2) or (α + β_2) regions at different temperatures. The solubility of hafnium in tantalum established by such a method at 900, 1100, 1300 and 1500°C is equal to 6, 8.8, 16 and 33 weight percent, respectively.

Figure 4 shows X-ray diffraction patterns of certain alloys. Composition and heat treatment are indicated to the left of the chart. The length of the line corresponds approximately to the line intensity in the X-ray diffraction pattern.

The X-ray diffraction patterns of tantalum in alloy No. 13 (80 percent Ta) show only lines for the β_2-phase. X-ray diffraction patterns for hafnium show only the lines for the α-phase. X-ray diffraction patterns for alloys Nos. 1-11 do not contain lines for the α-phase. In all of these alloys instead of α-phase α'-phase is present, i.e., supersaturated solid solution of tantalum in α-hafnium. On the X-ray diffraction patterns of alloys the line indices and the phase to which the particular line corresponds are also indicated. Tantalum solid solution in the high modification of hafnium (β_1-phase) is not preserved by quenching. This results in the formation of α'-phase. From the changes of the lattice parameter of the α'-phase of alloys tempered at 1500°C it was established that the boundary between the single phase β_1-region and the $\beta_1 + \beta_2$ two-phase region occurs at 22-23 wt percent of tantalum. /210

On the basis of these data a phase diagram was constructed for the hafnium-tantalum system in the solid state (fig. 5). The melting point of alloys was not determined. It can be seen from the diagram that tantalum sharply lowers the polymorphic transformation temperature in hafnium to 1020 ± 10°C, at which monotectoid equilibrium $\beta_1 \rightleftarrows \alpha + \beta_2$ takes place. The $\beta_1 + \beta_2$ two-phase region at 35-40 wt percent Ta extends to 1670°C. The maximum solubility of tantalum in α-hafnium is approximately 5 percent. The monotectoid alloy contains approximately 17 wt percent Ta. In titanium, zirconium and hafnium base alloys a new type of metastable phases was established, the so-called ω-phases. The review of work on these phases is given

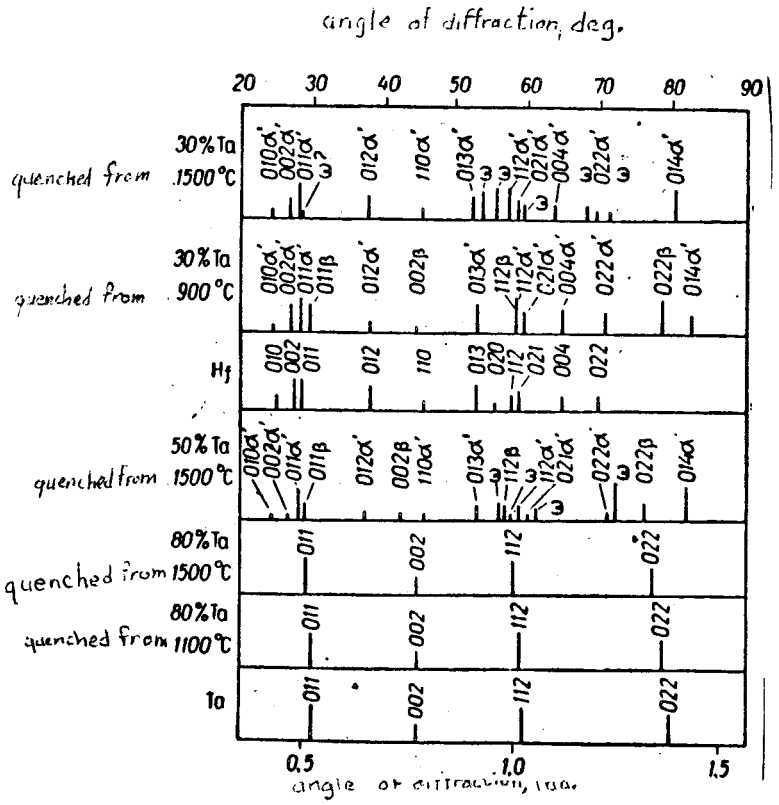

Figure 4. X-ray diffraction patterns.

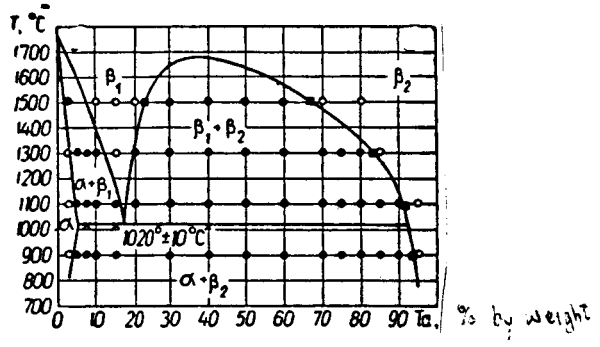

Figure 5. Phase diagram of hafnium-tantalum system in solid state.

in reference 18. The ω-phase in the alloys of the indicated systems forms only under the following conditions: (a) the alloy has an electron concentration n = 4.10-4.19; (b) the alloy is tempered from the β-region (body-centered

cubic lattice); (c) the α-phase, which has a closely packed hexagonal lattice, is the low temperature equilibrium phase. It was established that the ω-phase has a hexagonal lattice with three atoms in the unit cell, for which c/a = /211 0.612-0.63. The formation of the ω-phase increases the hardness and brittleness of the alloys.

The ω-phase was discovered in hafnium-tantalum alloys containing 10-20 wt percent Ta and tempered from 1100, 1300, 1500 and 1700°C (above the temperature of monotectoid equilibrium). The electron concentration of these alloys is 4.10-4.20. The X-ray diffraction patterns of tempered alloys in addition to α'-phase lines clearly show the lines of the ω-phase. Figure 4, for example, shows a scheme of the X-ray diffraction patterns of alloy No. 7 (30 percent Ta) tempered from 900 and 1500°C. In the former case the X-ray diffraction pattern does not show the ω-phase lines, since the tempering temperature is below the temperature of monotectoid equilibrium. At 1500°C two phases exist in equilibrium in this alloy ($\beta_1 + \beta_2$). Phase β_1 contains approximately 20 percent Ta which satisfies the condition for the formation of the ω-phase. The X-ray diffraction pattern of this alloy, quenched from 1500°C, clearly shows the lines of the ω-phase. In all cases with the ω-phase alloys also contain α'-phase, and in certain cases (high tantalum alloys) also the β_2-phase.

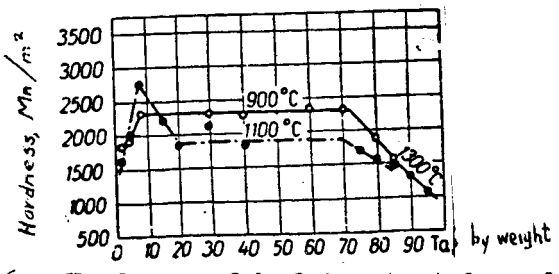

Figure 6. Hardness of hafnium-tantalum alloys annealed at 900 and 1100°C.

The hardness of alloys annealed at 900-1100°C is shown in figure 6. In the $\alpha + \beta_2$ two-phase region in the case of 900°C annealing hardness changes linearly, but at 1100°C it sharply increases at those concentrations of tantalum at which the solid ω-phase is formed.

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